

18.8100 14/18/40/60/530
 24.7500 1744/11/60, 1482, also 2108 26693
 1.1210 2808, 3008, 3108 also 2108 5/026/61/041/005/003/038
 B109/B102

AUTHORS: Al'tshuler, L. V., Kormer, S. B., Bakanova, A. A., Petrunin, A. P., Funktikov, A. I., Gubkin, A. A.

TITLE: Irregular conditions of oblique collision of shock waves in solids

PERIODICAL: Zhurnal eksperimental'noy i teoreticheskoy fiziki, v. 41, no. 5(11), 1961, 1382 - 1393

TEXT: On the basis of papers by V. Blikney, A. Taub (Sb. Voprosy raketnoy tekhniki, 1, 1951), L. D. Landau, Ye. M. Lifshits (Mekhanika sploshnykh sred - Mechanics of Continuous Media, Gostekhizdat, 1954), O. S. Ryzhov, S. A. Khristianovich (PMM, 22, 586, 1958), Ya. B. Zel'dovich, Gandel'man, and Ye. A. Feoktistova (DAN SSSR, 136, 1325, 1961) the authors describe a method of producing and recording irregular conditions for the collision of shock waves in solids. The experimental arrangement is shown in Fig. 2a. The detonation waves which enter the specimen at a slant cause shock waves with amplitudes of between 3 and $4 \cdot 10^5$ atm. Another arrangement allowed reaching shock waves of $1 - 1.8 \cdot 10^6$ atm. The parameters of the

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S/056/61/041/005/008/038
B109/B102

Irregular conditions of oblique

three-shock configuration forming as a result of the collision of the shock waves, are given for aluminum, lead, iron, and copper bodies. Near the critical angle at which a shock wave can still arise pressure was found to rise by from 6 to 8 times. When the waves have greater amplitudes, pressure in the collision region rises up to $4 \cdot 10^6$ atm in aluminum. In steel, copper, and lead it may even reach $7 \cdot 10^6$ atm if the waves collide at right angles. The results are analyzed by means of the method of the impact polars. It is shown that the picture with only one tangential discontinuity cannot be employed in describing the irregular conditions of the oblique collision of weak shock waves in the metal. The authors present a method of determining pressure and density behind the reflected wave front from the parameters of the three-shock configuration. Pressure and density for the collision of strong shock waves in aluminum were calculated as examples. It was found that the incident and reflected waves increase the density of aluminum up to 6.12 g/cm^3 . M. P. Speranskaya, N. S. Tenigin (deceased), A. N. Kolesnikova, M. S. Shvetsov, L. N. Gorelova, and M. V. Sinitsyn are thanked for assistance and information. There are 14 figures, 3 tables, and 9 Soviet references.

SUBMITTED: May 18, 1961
Card 2/3

25335

S/020/61/138/006/011/019
B104/B214

24,3950 also 2108

AUTHORS: Zel'dovich, Ya. B., Academician, Kormer, S. B., Sinitsyn,
M. V., and Yushko, K. B.

TITLE: An investigation of the optical properties of transparent
substances at superhigh pressures

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 138, no. 6, 1961
1333 - 1336

TEXT: The propagation of strong shock waves in transparent media permits
to study the properties of substances at pressures of some thousands or
millions of atmospheres (Zel'dovich et al., DAN 122, no. 1, 48(1958)).
At pressures not too high if the compressed substance remains transparent
throughout its thickness the refractive index may be determined geometri-
cally. The authors first studied water, plexiglass, and glass. A diagram
of the experimental set-up with which the reflection of light by the
shock wave can be determined, is shown in Fig. 1. The reflected rays
II - V were recorded by a fast photochronograph. Water was found to re-
main transparent under pressures of 89 - 144 thousand atmospheres. Glass
becomes opaque at a pressure of 200,000 atmospheres. The exact values
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25335

S/020/61/138/006/011/019
B104/B214

An investigation of the optical...

for water are collected in Table 1. In the discussion of the results the authors used the data of V. Raman and K. S. Venktaraman (Proc. Roy. Soc., 171, 137 (1939)) and gave the following relation for the temperature and density dependence of the refractive index: $n = 1.334 + 0.334(\rho - 1)$

$- 1.90 \cdot 10^{-5} T$ (1), T being in °C. Fig. 3 shows graphically a comparison of the values of n calculated by (1) with those determined by geometrical methods. The dotted line in this diagram corresponds to the Lorentz - Lorenz formula. The deviations of the results obtained photometrically can be partly explained by the increase in viscosity of water at high pressure. L. V. Al'tshuler (Ref. 6) had detected a decrease of the intensity of the reflected light at pressures above 115,000 atm and shown it to be related to the phase transformation at this pressure. This effect could not be detected by the present authors. They are of the opinion that water remains transparent up to 300,000 atm. A. G. Oleynik, V. N. Mineyev, and R. M. Zaydel' are mentioned. The authors thank V. P. Arzhanov, G. V. Krishkevich for carrying out the experiments and A. G. Ivanov, R. M. Zaydel', A. G. Oleynik, and V. N. Mineyev for valuable discussions. There are 3 figures, 1 table, and 10 references: 5 Soviet-

Card 2/5

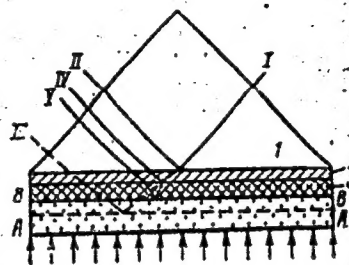
An investigation of the optical...

bloc, and 5 non-Soviet-bloc.

SUBMITTED: March 30, 1961

Fig. 1: Experimental set-up.

Legend: I) incident ray. II) and III) light reflected from the stationary boundary between plexiglass and water. IV) light reflected from the front of the shock wave. V) light reflected from the moving boundary between compressed water and compressed plexiglass. 1) plexiglass prism. 2) water in front of the shock wave front. 3) water compressed in the shock wave.



Card 3/5

35557

S/056/62/042/003/007/049
B104/B102

24.5300 18.8100

AUTHORS: Kormer, S. B., Funtikov, A. I., Urtin, V. D., Kolesnikova, A. N.

TITLE: Dynamic compression of porous metals and the equation of state with variable specific heat at high temperatures

PERIODICAL: Zhurnal eksperimental'noy i teoreticheskoy fiziki, v. 42, no. 3, 1962, 686 - 702

TEXT: The dynamic compression of Al, Cu, Pb, and Ni with relative densities between $m = 1$ and $m = 4$ ($m = \rho/\rho_{00}$, where ρ_0 = density of the compact material, ρ_{00} = density of the porous material) was studied in the pressure range of $0.7 \cdot 10^{12}$ - $9 \cdot 10^{12}$ dynes/cm². A polyempirical interpolated equation of state is developed which takes account of the specific heat variations and the density and temperature dependence of the Grüneisen coefficient

$$P = P_s(\rho) + \frac{3\gamma(\rho) + z(\rho, T)}{1 + z(\rho, T)} \rho R (T - \hat{T}) + g(\rho) \rho \frac{b^3}{\beta(\rho)} \ln \chi \frac{\beta(\rho) T}{b}, \quad (14)$$

$$E = E_s(\rho) + \frac{2 + z(\rho, T)}{1 + z(\rho, T)} \cdot \frac{3}{2} R (T - \hat{T}) + \frac{b^3}{\beta(\rho)} \ln \chi \frac{\beta(\rho) T}{b}. \quad (15).$$

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Dynamic compression of...

S/056/62/042/003/007/049
B104/B102

The equations of state of Mie-Grüneisen, and the equation of state with the electronic specific heat components, are special cases of (14), (15). Solid metals and metal vapors can be described by these equations of state. The shock adiabats calculated for metals of different densities are in good agreement with experimental data. The gas pressure and the lattice energy can be determined from the equation of state by a limiting process. The electronic analog of the Grüneisen coefficient is found for Cu and Ni, and estimated for Pb and Al. Symbols used in the equations: γ is the Grüneisen coefficient, $\beta(e)$ the electronic specific capacity, $z = 1RT/c_x^2$, where 1 is a quantity to be determined experimentally.

K. K. Krupnikov, B. N. Ledenev, L. V. Al'tshuler, A. A. Bakanova, R. F. Trunin, V. N. Zharkov, V. A. Kalinin, and N. N. Kalitkin are mentioned. S. V. Yezhkov, G. M. Yesin, and V. I. Yefremov are thanked for assisting with experiments, Yu. A. Glagoleva and L. T. Popova for assisting with calculations, L. V. Al'tshuler, A. A. Bakanova, K. K. Krupnikov, and R. F. Trunin for discussions, and Ya. B. Zel'dovich, V. P. Kopyshchev, Yu. P. Rayzer, and K. A. Semendyayev for consultations. There are 11 figures, 5 tables, and 22 references: 15 Soviet and 7 non-Soviet. The four most recent references to English-language publications

Card 2/3

Dynamic compression of...

S/056/62/042/003/007/049
B104/B102

read as follows: R. G. McQueen, S. P. Marsh, J. Appl. Phys., 31, 1253,
1960; J. S. Dugdale, D. K. McDonald, Phys. Rev., 89, 832, 1953;
J. J. Gilvarry, Phys. Rev., 96, 934, 944; 99, 550, 1955; Handbook of
Chemistry and Physics, 37ed Chemical Rubber publishing Co. Cleveland,
1955 - 1956.

SUBMITTED: August 10, 1961

Card 3/3

L 13950-65 AS(mp)-2/AEDC(a)/ESD(gs)
ACCESSION NR: AP4047885

S/0056/64/047/004/1202/1213

AUTHOR: Kormer, S. B.; Sinitay*n, M. V.; Funtikov, A. I.; Urlin, V. D.; Blinov, A. V. B

TITLE: Investigation of the compressibility of five ionic compounds at pressures up to 5 Mb

SOURCE: Zhurnal eksperimental'noy i teoreticheskoy fiziki, v. 47, no. 4, 1964, 1202-1213

TOPIC TAGS: compression, high pressure, compressibility, ionic crystal

ABSTRACT: The dynamic compression of LiF, NaCl, KCl, KBr, and CsBr ionic crystals of normal and reduced density is investigated for a wide range of pressures, densities, and temperatures. The highest pressure attained was 5 Mb, and the maximum compression ratio (density/reduced density) was 3.4. The experimental data can be described by an equation of state in which the temperature change due to specific heat and the thermal excitation of electrons is taken into account.

Card 1/2

L 13950-65

ACCESSION NR: AP4047885

D
The data obtained indicate an anomalous behavior of NaCl, KCl, KBr, and LiF crystals during shock compression. For the first three crystals, density discontinuities were detected in the liquid state. It is suggested that this may be due to a change in the coordination number which occurs during the same length of time in which a shock wave is propagated along a sample. Orig. art. has: 7 figures, 4 tables, and 4 formulas.

ASSOCIATION: none

SUBMITTED: 18Apr64

ENCL: 00

SUB CODE: SS, ME

NO REF SOV: 012

OTHER: 004

ATD PRESS: 3133

Card 2/2

L 12407-55 EPA(s)-2/EPA/EMT(m)/EPF(c)/NTR/EMP(j) Pc-li/Paz-li/Pr-li/Ps-li/
Pt-lo RPL/AFWL/SSD/ASDC(b)/Pa-li 181/JW/JWD/RM

ACCESSION NR: AP4047941

5/0020/64/158/005/1051/1053

AUTHOR: Zal'dovich, Ya. B. (Academician);
Krishkevich, G. V.; Yushko, K. B.

Korner, S. B.

TITLE: Study on the smoothness of a detonation front in a liquid explosive

SOURCE: AN SSSR. Doklady*, v. 158, no. 5, 1964, 1051-1053

TOPIC TAGS: liquid explosive, explosive, detonation, detonation front, nitro, so d, dichloroethane

ABSTRACT: The smoothness of a detonation front propagating in a stoichiometric mixture of nitric acid-dichloroethane mixture was studied by recording the pressure in a

prism having a refractive index differing considerably from that of the explosive. The detonation was initiated with a 50/50 trotyl/hexogen charge 200 mm long and 120 mm in diameter. A detonation velocity

Card 1/2

L 12h07-65

ACCESSION NR: AP4047941

of 6.2 ± 0.1 km/sec and a reflection coefficient of $1.8 \pm 0.1\%$ were measured at an explosive temperature of -2°C . Comparison of the reflection coefficient for a Chapman-Jouguet detonation showed that the detonation was normal. The reflection was mirror-like and was sharply delineated. It was concluded that in stoichiometric HNO_3 -dichloroethane mixtures, a normal detonation wave is obtained with a plane shock front preceding the reaction front, and that inhomogeneities are absent. This result is in contrast to previous findings by Dremmin, Rozanov, and Trofimov, who found inhomogeneities in the reaction front. Orig. art. has: 3 figures.

ASSOCIATION: none

SUBMITTED: 20Jun64

ENCL: 00

SUB CODE: WA

NO REF SOV: 010

OTHER: 000

ATD PRESS: 3127

Card 2/2

L 01719-85
EST(E)/EXP(W)/EAT(d)/T/EXP(L)/EXP(L)/EXP(L)/EXP(L)

Forman, J. E.; Puntikov, A. I.

Impact compression of ferrosilicon and the possible exsolution of the

"Zhurnal AN SSSR. Izvestiya. Fizika Zemli, no. 5, 1965, 1-3

TOPIC TAGS: high pressure, iron alloy, silicon alloy, earth core, impact testing

1. The impact compression of iron and silicon alloy has been investigated as a solid representing the composition of the earth's core. The material tested was industrial ferrosilicon with a composition of 81.3% Fe, 17.4% Si, and 1.1% C, representing a solid solution of silicon in alpha-iron with inclusion of graphite. The specific gravity of the material was 7.4.

the shock wave were determined, and the density under compression was computed at pressures ranging from 0.48 to 3.3 megabars. It was found that the velocity of sound waves computed for the ferrosilicon at 4000K and the appropriate pressure agrees with geophysical data somewhat better than the value for pure iron. It is

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L-61719-65

ACCESSION NR: AP5017788

0
It is suggested that an outer core of iron-silicon alloy with about 20% silicon there-
fore corresponds to most of the geophysical data on the properties of this outer
core. Results of the present studies indicate that the light constituent in the
alloy cannot exceed 20%. In a study of pyrite, containing 60% Fe (with a sp gr
of 4.74), the density under impact compression proved to be only 8.9 g/cm³ at
100 kbars, instead of 11.3 as required according to Bullen's calculations.
References: 3 figures and 1 table.

ASSOCIATION: none

SUBMITTED: 16Nov64

ENCL: 00

SUB CODE: ES, ME

NO REF SCV: 008

OTHER: 006

12
Card 2/2

L 41067-65 EWP(m)/EWT(1) Pd-1

ACCESSION NR: AP5010495

UR/G056/65/048/004/1033/1049

Author: Gerasimov, S. B.; Sinitsyn, M. V.; Kirillov, G. A.; Uralin, V. D.

TITLE: Experimental investigation of temperatures and fusion curves of shock-compressed NaCl and KCl under pressures up to 700 kbar

SOURCE: Zhurnal eksperimental'noy i teoreticheskoy fiziki, v. 48, no. 4, 1965, pp. 1111-1114.

TOPIC TAGS: shock wave, shock wave front, shock wave temperature, shock wave front temperature, ultrahigh pressure dynamics, ultrahigh temperature dynamics, ultrahigh temperature effect, ultrahigh pressure effect, shock wave fusion, NaCl shock wave treatment, KCl shock wave treatment

ABSTRACT: Temperature determinations were made at the 4780 and 6250 Å wavelengths on the basis of the brightness of the shock wave fronts as compared to the brightness of the reference light source. The measurements were carried out on NaCl and KCl crystals (40 x 40 x 20 mm). The shock wave in the crystals was created by a gas gun. The plate of the crystal was placed in the center of the gun barrel. The shock wave front was observed through a microscope. The temperature was determined by the method of color comparison. The interference from the air on the surface of the crystal was eliminated by the use of a special technique.

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L 41067-65

ACCESSION NR: AP5010495

investigated front. The fusion curves of both crystals were plotted in order to account for the effect of fusion on the temperature. These curves confirmed that the front actually takes place. For NaCl fusion started at 3500K and the liquid state was fully formed. For KCl fusion started at 3000K and 330 Kbar for the start of fusion and 4100K and 400 Kbar for full fusion. The thermal capacity of the solid phase was relatively constant, with values somewhat above those of NaCl and KCl. The fusion curves agreed with those of Clark (S. Clark, *J. Chem. Phys.*, 31, 1959, 1526). The entropy jump remained virtually constant over the entire pressure range; the volume jump, however, showed a significant increase from 20-25% at zero pressure to 40% at 400 Kbar, and for KCl the increase was 4% at 400 Kbar. The effect of the increase in the pressure on the barrier occurring with higher pressure was not overcome by the fact that the properties of a liquid under high pressure, at least at the temperature of fusion, are less distinct from those of a solid than under atmospheric pressure. The data obtained in the experiments failed to confirm the assumption that a phase change behind a shock wave might lead to a wave split. Orig. art. has: 10 figures and 14 formulas.

[FP]

Card 2/3

SUBMITTED: 5 NOV 64

KORMER, S.B.; SINITSYN, M.V.; KIRILLOV, G.A.; POPOVA, L.T.

Experimental determination of the coefficient of light absorption
by shock-compressed NaCl. The mechanism underlying absorption and
conductance. Zhur.eksp.i teor.fiz. 49 no.1:135-147 J1 '65.
(MIRA 18:8)

ACC NR: AP6036755

SOURCE CODE: UR/0020/66/171/001/0065/0068

AUTHOR: Zel'dovich, Ya. B. (Academician); Kormer, S. B.; Krishkevich, G. V.; Yushchko, K. B.

ORG: none

TITLE: The problem of the smoothness of the detonation front in a liquid explosive

SOURCE: AN SSSR. Doklady, v. 171, no. 1, 1966, 65-68

TOPIC TAGS: shock wave, detonation front, detonation front profile, detonation front reflectivity, detonation front reflecting loss, liquid explosive

ABSTRACT: An analytical investigation of the light reflectivity of the detonation front in a liquid explosive (a mixture of nitric acid and dichloroethane) is presented, to explain the deviation of the experimental values of the reflection factor from the values calculated on the basis of the change of the refractive index in the wave front. The analysis uses earlier experimental data and yields a semi-quantitative description of the phenomenon as based on the wave theory of light reflection. The difference between the observed and calculated values of the reflection index, the analysis shows, can be ascribed to a certain degree of roughness on the detonation front comparable to the wavelength of the incident light. The degrees of roughness and the corresponding losses of reflected light intensities within the full range from purely specular to fully diffuse reflection were

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UDC 532.5+535.8

ACC NR: AP6036755 (A)

established. Conversely, the measured intensities of reflected light and dependence of the diffusely reflected portion on the angle of incidence characterize the degree and the average period of the roughness of the detonation front. The character of the roughness proved to be stationary under given conditions of detonation, while perturbations of higher orders leveled off very quickly. The deviation of the detonation front from a perfect specular surface is considered proven. The actual origin of the deviation, however, remains to be determined. At present, two explanations are considered possible: either it is a phenomenon resembling that observed earlier with gaseous detonation and only modified for the higher density of liquids; or it is initiated by inhomogeneities in the zone of chemical reaction, although no feedback of these fluctuations on the process of reaction has been observed. The use of the laser beam as a light source is being considered for a more detailed investigation of the profile of the detonation surface. Orig. art. has: 3 figures and 1 table.

SUB CODE: 20/ SUBM DATE: 18Jul66/ ORIG REF: 004/ AYD PRESS: 5107

Card 2/2

ACC NR: APPROVED FOR RELEASE: 06/14/2000 CIA-RDP86-00513R000824710005-4

AUTHOR: Kormer, S. B.; Yushko, K. B.; Kirshkevich, G. V.

ORG: none

TITLE: Dependence of the refractive index on the density of the solid and liquid phases of shock-compressed ionic crystals. Relaxation time of phase transformation under shock compression

SOURCE: Zhurnal eksperimental'noy i teoreticheskoy fiziki. Pis'ma v redaktsiyu, v. 3, no. 2, 1966, 64-69

TOPIC TAGS: ionic crystal, refractive index, alkali halide, compression shock wave, shock wave front

ABSTRACT: The refractive indices of shock-compressed alkali-halide compounds were investigated. For LiF, which remains transparent in the investigated range of pressures up to $P \approx 700$ kbar, the refractive index was determined directly from the paths of the rays in the compressed matter. For NaCl, CsBr, KCl, and KBr crystals, which become opaque behind the shock-wave front, the refractive indices were determined by Fresnel's formulas from the experimentally-measured coefficients of reflection of natural light incident on the front of the shock wave. The dependence of the refractive index on the degree of compression σ (where $\sigma = \rho/\rho_0$ is the running density and ρ_0 the density at $T = 300^\circ\text{K}$ and $P \approx 0$) for the crystals LiF, NaCl, and

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UDC: none

ACC NR: AP7007678

state changes the refractive index by about 1.5 times more than in the solid state. In investigating the reflectivity of the shock-wave front in the solid phase of KCl and KBr it was noted that at $P \approx 140$ kbar the reflection coefficient is 2 - 3 times smaller than that corresponding to a relation of the type (1) for $n(\sigma)$, with values of $dn/d\sigma$ that follow from whereas at $P \approx 200$ kbar for KCl and 260 kbar for KBr the obtained results are close to those expected. We recall (see Sec. 1 and the table) that for other crystals the results of the measurements were in satisfactory agreement with earlier data. It is natural to relate the indicated difference with the polymorphic transformation of KCl and KBr into the CsCl structure, which occurs at $P \approx 20$ kbar assuming that up to $P \leq 140$ kbar the phase transformation of KCl and KBr occurs after a time $\tau > 10^{-11}$ sec, the light will be reflected from a layer of matter situated on the front of the shock wave in a metastable state (point 1, Fig. 2), corresponding to the dynamic adiabat of the first phase 6). Since the latter is steeper than the adiabat of the second phase, a smaller density jump on the shock-wave front corresponds also to a smaller refractive index. The non-equilibrium states of the first phase of KCl and KBr (point A, Fig. 2), determined from the shock-wave velocity, from the dependence (1) with $dn/d\sigma$ as given in the table, and from the measured reflection coefficient, are shown in Fig. 2. For KCl the point obtained lies somewhat to the left of the first-phase adiabat calculated from the equation of state. With increasing pressure, the temperature increases (for KCl, $T = 1300^\circ\text{K}$ at $P = 136$ kbar and $T = 2100^\circ\text{K}$ at $P = 200$ kbar), the relaxation time decreases, and the phase transformation takes place in a layer thinner than $\lambda/2\pi$ (λ = wavelength of the incident light). In this case the refractive index will correspond to the

Cord 3/5

ACC NR: AP7007678

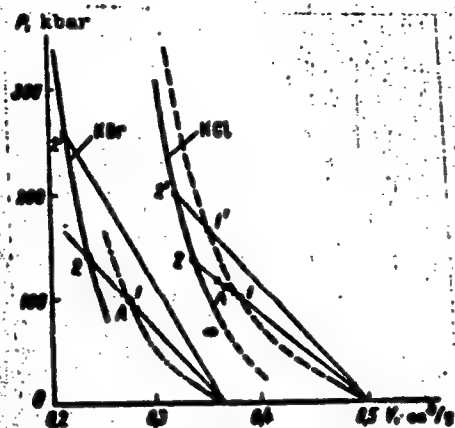


Fig. 2. Equilibrium and non-equilibrium dynamic adiabats of KCl and KBr. — calculated after [12,3], ----- calculated after [3], -.-.- interpolation, -o-o-o present experiments.

Cord 4/5

ACC NR: AP7007678

total jump in volume behind the front of the shock wave (point 2', Fig. 2). Considering that the values of $dn/d\sigma$ obtained for phase II turned out to be close to the values for phase I, the measured reflection coefficients were close to those expected. Thus, upon shock compression with $P = 200 = 260$ kbar, the polymorphic transition in KCl and KBr takes place within a time $\tau < 10^{-11}$ sec. (The polymorphic transition, interesting, has no effect on the $n(\sigma)$ dependence of these ionic crystals.) The same time is characteristic also of melting in the shock-wave front, since the refractive index (reflection coefficient) experiences a jump at pressures corresponding to the transition of the solid phase into liquid (see Fig. 1). Orig. art. has: four formulas.

SUB CODE: 20 / SUBM DATE: 01Nov65 / ORIG REF: 005
OTH REF: 008

Card 5/5

SIVASH, Konstantin Mitrofanovich, kand. med. nauk; KORMER, M.B., red.;
BUL'DYAYEV, N.A., tekhn. red.

[Osteoarticular tuberculosis; prevention and treatment]
Kostno-sustavnoi tuberkulez; profilaktika i lechenie. Moskva,
Medgiz, 1961. 65 p. (MIRA 15:3)

(BONES—TUBERCULOSIS)

KORMER, V. A.
USSR/Chemistry

Card 1/1

Authors : Chelpanova, L. F.; and Kormer, V. A.

Title : Synthesis and conversion of alpha-glycols of the ethylene series.
Part 2.-

Periodical : Zhur. Ob. Khim. 24, Ed. 5, 849 - 852, May 1954

Abstract : Report describes conversions of a trans-isomer 2-methyl-3, 5-diphenyl-pentene-4-diol-2, 3 in the presence of 14 and 20% alcohol solutions of sulfuric acid during heating. This glycol was obtained through catalytic hydrogenation of an acetylene glycol - 2-methyl-3, 5-diphenyl-pentyne-4-diol-2, 3. By heating the trans-isomer of the ethylene glycol (melting point 85 - 86°) with a 14% alcohol solution of H₂SO₄ to 55 - 60° the authors obtained about 70% of the basic glycol and about 5% of a yellow-orange colored substance (oily substance) the properties of which were not investigated. Five USSR references. Graph.

Institution: The Lenseviet Technological Inatitute, Leningrad, USSR

Submitted : October 20, 1953

CHELPAKOVA, L.F.; KORMER, V.A.

Synthesis and conversion of ethylene α -glycols. Part 4.
2,4-diphenylbutene-3-diol-1,2. Zhur.ob.khim.no.8:1513-1516
Ag '55. (MLRA 9:2)

1.Leningradskiy tekhnologicheskiy institut imeni Lenseveta.
(Butene)

SOV/51-7-2-26/34

AUTHORS: Petrov, A.A., Yakovleva, T.V. and Kormer, V.A.

TITLE: Infrared Spectra of Certain Di-Substituted Allene Hydrocarbons
(Infrakrasnyye spektry nekotorykh dvuzameshchennykh allenovykh
uglevodorodov)

PERIODICAL: Optika i spektroskopiya, 1969, Vol 7, Nr 2, pp 267-271 (USSR)

ABSTRACT: The authors obtained the infrared transmission spectra of the following
nine allenes:
heptadiene-2,3 (curve 1 in a figure on p 268);
nonadiene-2,3 (curve 2);
7-methyloctadiene-2,3 (curve 3);
6,6-dimethylheptadiene-2,3 (curve 4);
octadiene-3,4 (curve 5);
nonadiene-3,4 (curve 6);
7-methyloctadiene-3,4 (curve 7);
decadiene-3,4 (curve 8);
7,7-dimethyloctadiene-3,4 (curve 9).
The frequencies of the nine compounds are listed in a table on pp 269-270.
These hydrocarbons were prepared by reaction of lithium alkyls and
vinylalkylacetylenes. The spectra were recorded by means of an

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Infrared Spectra of Certain Di-Substituted Allene Hydrocarbons

SGV/51-7-2-26/34

IKS-14 spectrophotometer using an NaCl prism up to 1800 cm^{-1} and an LiF prism for higher wave numbers. The samples were in the form of layers 0.03 mm thick. The most characteristic and intense bands observed in the spectra of all these hydrocarbons were the bands due to the allene group at $1960\text{--}1965\text{ cm}^{-1}$ and due to non-planar deformational vibrations of the group $\text{C}=\text{C}=\text{CH--}$ at $870\text{--}875\text{ cm}^{-1}$. Other absorption bands are briefly discussed. There are 1 figure, 1 table and 4 references, 1 of which is Soviet, 1 translation from English into Russian and 2 French.

SUBMITTED: February 23, 1959.

Card 2/2

5(3)

AUTHORS:

Chelpanova, L. F., Kormer, V. A.

SOV/79-29-7-52/83

TITLE:

Synthesis and Transformation of the α -Glycols of the Ethylene Series (Sintez i prevrashcheniye α -glikoley etilenovogo ryada). VII. Transformation of 1,2,4-Triphenylbutene-3-diol-1,2 and 2,3-Dimethyl-5-phenylpentene-4-diol-2,3 (VII. Prevrashcheniye 1,2,4-trifenilbuten-3-diola-1,2 i 2,3-dimetil-5-fenilpenten-4-diola-2,3)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 7, pp 2348-2354 (USSR)

ABSTRACT:

It is evident from recently published reports (Refs 1-3) that ethylene- α -glycols in an acid medium are able, by isomerization, to form substituted dihydrofuran, besides giving aldehydes and ketones. In the present investigation, the authors tried to isomerize the glycols 1,2,4-triphenylbutene-3-diol-1,2 (I) and 2,3-dimethyl-5-phenylpentene-4-diol-2,3 (II) in solutions of 20% alcoholic and 30% aqueous sulfuric acid at 60-100°. On heating (I) at 60-70° with 20% alcoholic sulfuric acid an oily product separated. Its properties and analysis indicated it to be an aldehyde of the ethylene series. Oxidation of the product yielded benzoic and diphenylacetic acid, which is in accordance with (III). The ultraviolet absorption bands of the product

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Synthesis and Transformation of the α -Glycols of the SOV/79-29-7-52/8
Ethylene Series. VII. Transformation of 1,2,4-Triphenylbutene-3-diol-1,2 and
2,3-Dimethyl-5-phenylpentene-4-diol-2,3

were characteristic for styryl and carbonyl groups. Heating the same glycol with 30% aqueous sulfuric acid also gave (III) in 50% yield as well as a crystalline product (15%) with the empirical formula $C_{22}H_{18}O$ to which the structure (V) was tentatively ascribed. A maximum in the ultraviolet spectrum of (V) is due to conjugation of the double bond with the phenyl group (Fig 1). As shown in a table, an infrared absorption spectrum of (V) indicated it to be dihydrofuran-2,5. The hitherto unknown diol (II) was prepared by hydrogenating the corresponding acetylene glycol (Ref 7) in the presence of colloidal palladium. Thus, two geometric cis and trans isomers of this ethylene glycol were obtained. Treatment of the diol (II) with 20% alcoholic sulfuric acid at 50° and with 30% aqueous sulfuric acid at 90-100° yielded a substance with the empirical formula $C_{13}H_{16}O$. The structure of a 4,5,5-trimethyl-2-phenyl-dihydrofuran-2,5 (VI) was proposed for this compound,

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Synthesis and Transformation of the α -Glycols of the *NOV/79-29-7-52/83*
Ethylene Series. VII. Transformation of 1,2,4-Triphenylbutene-3-diol-1,2 and
2,3-Dimethyl-5-phenylpentene-4-diol-2,3

which is consistent with its properties and spectroscopic data.
The conversion of the diol (I) into the diol (II) is shown in
scheme 1 and discussed. There are 2 figures, 1 table, and
14 references, 12 of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskii institut imeni Lenoaveta
(Leningrad Technological Institute imeni Lenoavet)

SUBMITTED: December 31, 1957

Card 3/3

5(3)

AUTHORS:

Petrov, A. A., Kormer, V. A.

SOV/20-125-5-24/61

TITLE:

On the Combination of Lithium Ethyl and Lithium
Butyl with Vinyl-alkyl Acetylenes (O prisoyedinenii
litiy-etila i litiy-butila k vinilalkilatsetilenam)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 5,
pp 1041-1043 (USSR)

ABSTRACT:

There are only few data available in publications on the combination of lithium-organic compounds to carbon multiple bonds (Refs 1 - 3). Monomeric combination products are formed only by aryl-olefines. The radical reacts here with the less substituted final carbon atom. If lithium-organic compounds act upon olefines and diolefines, a telomerization takes place. However, substances can be isolated from the reaction mixture after the hydrolysis or after the treatment with CO₂ which, according to their composition, correspond to simple adducts. In the case of diolefines the combination of lithium alkyls apparently occurs according to the same rule. Primary adducts have here, however, apparently a tautomerism. Accordingly, a further telomerization yields substances

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On the Combination of Lithium Ethyl and Lithium
Butyl with Vinyl-alkyl Acetylenes

SOV/20-125-5-24/61

with a normal and with an isostructure. The production of the latter is favored by a temperature drop. The experiments of the authors showed that vinyl-alkyl acetylenes react with lithium ethyl and lithium butyl at a ratio of 1:1 with the formation of hydrocarbons C_nH_{2n-2} and a resinified residue (Table 1). Figure 1 shows the infrared spectra of the hydrogenation products (recorded with the aid of T. V. Yakovleva). They proved to be identical with those of n-heptane and n-octane. Hydrocarbons with a normal structure were obtained by hydrolysis and hydrogenation of two further adducts. Thus, it was detected that lithium alkyls combine with vinyl-alkyl acetylenes in a 1.4-position. The lithium atom migrates to the triple bond. Apparently, no lithium-organic compounds with one lithium atom at the simple bond are produced in the course of the reaction, otherwise compounds with a triple bond would be bound to occur among the polymers. However, no frequencies of a triple bond were detected in the infrared spectrum of the polymer (Fig 1:3). The frequency of a double bond occurs in this spectrum,

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On the Combination of Lithium Ethyl and Lithium
Butyl to Vinyl-alkyl Acetylenes

SOV/20-125-1-24/61

apparently in the grouping $-\text{CH}=\text{CH}-$, since intense absorption takes place within the range of deformation frequencies at 964 cm^{-1} . The last-mentioned grouping is most likely to be formed by the isomerization of the Allen system in the polymer. The above-discussed reaction is a new method of producing the least accessible and investigated group of Allen hydrocarbons with almost any desired position of the Allen group in the middle of the carbon chain. There are 1 figure, 1 table, and 7 references, 3 of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskii institut im. Lensovet
(Leningrad Institute of Technology imeni Lensovet)

PRESENTED: December 11, 1958, by B. A. Arbuzov, Academician

SUBMITTED: November 24, 1958

Card 3/3

5 (2,3)

AUTHORS:

Petrov, A. A., Korner, V. A.

SOV/20-126-6-37/67

TITLE:

On the Addition of Lithium Diethyl and Lithium Dibutyl Amide to Vinyl Acetylene and to Vinyl Alkyl Acetylenes (O prisoyedinenii litydietyl- i litydibutilamidov k vinilatsetilenu i vinilalkilatsetilenam)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 6, pp 1278 - 1281 (USSR)

ABSTRACT:

Only few data are available in publications concerning the subject mentioned in the title (Refs 1-3). In the present paper it is proved that the adducts of amines (diethyl and dibutyl amines) to vinyl acetylene hydrocarbons form by treating the addition products of the lithium dialkyl amides to these hydrocarbons with water. The mentioned alkyl diamides react at room temperature and under normal pressure. This reaction has hitherto not been described. According to the nature of vinyl acetylene hydrocarbon and the amide various products form from the corresponding reaction. Vinyl acetylene forms amines (III) with an acetylene end group (in the case of diethyl amine with a 20% yield) without any side processes. Besides polymers (25-30%) vinyl methyl acetylene produces mainly the dimer (IV) with a

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On the Addition of Lithium Diethyl and Lithium
Dibutyl Amide to Vinyl Acetylene and to Vinyl
Alkyl Acetylenes

SOV/20-126-6-37/67

yield of approximately 40%. Amines form only in very low yields (5%), they have different structure according to the nature of the amide: in the case of the addition of lithium diethyl amide an amine forms with an acetylene end group (V) in the case of the lithium dibutyl amide an allene amine compound (VI) is formed (see scheme). Vinyl ethyl acetylene furnishes allene amines of the type (VI) with lithium dialkyl amides (45-55%). The dimer amount does not surpass 10%. The structure of the amines was determined above all by their infrared spectra (Fig 1). Identities with already known substances were found in this connection (Ref 4). Moreover, the structure of the amines was determined by hydrogenation on colloidal palladium (Ref 5). In the infrared spectrum of the dimer of vinyl-methyl acetylene the absorption in the range of from 964 cm^{-1} indicates that the double bond is formed by a —CH=CH— group. (Fig 1 : 5). According to all these data the dimer may be ascribed the formula: 6-methyl-nonene-3-diine-1,8 (VI). The dimer of vinyl-ethyl-acetylene has an analogous structure. It is most probable that the

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On the Addition of Lithium Diethyl and Lithium
Dibutyl Amide to Vinyl Acetylene and to Vinyl Alkyl
Acetylenes

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dimers form due to the addition of their metallization products to vinyl acetylenes. In this connection the multiple bonds are shifted to the end of the chain under the effect of the lithium dialkyl amides. Table 1 gives the constants of the produced substances. Thus, it was found that lithium dialkyl amides may be added to the vinyl acetylenes similar to the lithium alkyls: the radical enters position 4 (Ref 7). In both cases the reaction probably takes place according to the radical mechanism. There are 1 figure, 2 tables, and 9 references, 4 of which are Soviet.

PRESENTED: March 4, 1959, by B. A. Arbuzov, Academician

SUBMITTED: February 28, 1959

Card 3/3

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5/18/60/000/000/001/007
ACU/ACQ

Author: W. J. Samoilov, V. I. Isakov, L. G. Priklet, D. P. Gerasimov, V. A. Gerasimov

Title: The Properties of SN-3 (SN-3) - a New Synthetic Isoprene Rubber

Source: Khimicheskaya, 1960, No. 3, pp. 1 - 5

The author states that in the last decade synthetic rubber of high elasticity was produced both by the USSR and the USA. A list of some of the types which were synthesized is submitted (p. 3 - 7). It is pointed out that all isoprene rubbers correspond to some degree to natural rubber, depending on the nature of the catalyst and the polymerization method. SN-3 was synthesized in the USSR in 1957 - 1958. SN-3 obtained with a complex modified catalyst was shown not to differ significantly in its structure from natural rubber and SN-3. It is quite similar to them in its technological and physico-mechanical properties. The structure of the rubber was determined by the infrared spectroscopy method. The detailed description of the structure is given and Table 1 shows the data of the analysis of the natural rubber and SN-3. Its physico-mechanical properties are discussed. It was found that the SN-3

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Rubber of a given composition exhibits at about the same rate as natural rubber and in this way differs from the quickly-vulcanizing liquid isoprene rubber. The elevated rate of vulcanization in the former is probably explained by the presence of residual catalyst. SN-3 is close to natural rubber in its properties (see Table 1). It was also found that rubbers produced with a complex modified catalyst have a more uniform structure, better technological properties and a higher tensile strength than those produced with a simple catalyst. This is due to the high-molecular weight of the isoprene rubber. The authors think that SN-3 due to its many valuable properties is of great significance to the tire and rubber industries. There are 6 tables, 1 figure and 9 references; 8 Soviet and 3 Eng-lish.

Annotation: Vsesoyuzny Institut khimicheskogo kumchstva im. S. V. Lebedeva (All-Union Institute for Synthetic Rubber Invent. S. V. Lebedev)

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69673

5.37.00(B)
AUTHORS: Petrov, A. A., Kormer, V. A.

S/153/60/003/01/029/058
B011/B005

TITLE: On the Addition of Lithium Alkyls on Divinyl Acetylene¹

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1960, Vol 3, Nr 1, pp 112-114 (USSR)

TEXT: The authors' experiments showed that lithium alkyls readily react with divinyl acetylene. Industrial divinyl acetylene with small impurities of acetylenyl divinyl and about 20% of xylene, lithium ethyl, 2 isomeric lithium butyls, and lithium amyl were used for this purpose. With each of the lithium alkyls mentioned, divinyl acetylene could form 6 different adducts (1,2-, 1,4- and 1,6-addition) with triene- or enine groups. The authors, however, expected that only vinyl-allene hydrocarbons would form on the basis of the rules established before: $\text{CH}_2=\text{CH}-\text{CH}=\text{C}=\text{CH}-\text{CH}_2-\text{R}$ (after treating the adducts with water). The acetylenyl divinyl present as an admixture would not take an active part in the formation of monomer products. The experiments confirmed this assumption. Only 1,3,4-triene hydrocarbons were formed. They contained only traces of acetylene compounds. The structure of the reaction products was proved on the basis of their infrared and ultraviolet spectra as well as by hydrogenation to saturated hydrocarbons. A normal structure of the hydrocarbons used

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Acetylene

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was proved in all cases. There were no fully conjugate trienes. Table 1 presents the constants of the vinyl allenes obtained for the first time. Vinyl allenes have much smaller refractive indices than 1,3,5-trienes. The figure (p 114) shows the infrared spectra of trienes recorded by an IKS-14 spectrophotometer. The spectra will be described and analyzed in a separate paper. There are 1 figure, 2 tables, and 5 references, 4 of which are Soviet.

ASSOCIATION: Leningradskiy tekhnologicheskii institut im. Lensovet; Kafedra organicheskoy khimii (Leningrad Technological Institute imeni Lensovet; Chair of Organic Chemistry)

SUBMITTED: April 13, 1959

Card 2/2

REYKH, V.N.; SAMOLETOVA, V.V.; IVANOVA, L.S.; PERINGHE, D.P.; KORMER, V.A.

Properties of the SKI-3, new synthetic isoprene rubber. Kauch. i
rez. 19 no.3:1-5 Mr '60. (MIRA 13:6)

1. Vsesoyuznyy institut sinteticheskogo kauchuka im. S.V.Lebedeva.
(Rubber, Synthetic) (Isoprene)

. 5.3700

77386
SOV/79-30-1-47/78

AUTHORS: Kormer, V. A., Petrov, A. A.

TITLE: Investigations in the Field of Conjugated Systems. CXIII. Concerning the Addition of Alkylolithium Compounds to Vinylalkylacetylenes (Enyne Compounds, XXXVI)

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 1, pp 216-219 (USSR)

ABSTRACT: Continuing their studies of the addition of electrophilic and nucleophilic reagents to vinylacetylenes of various structure (ZhOKh., 1950, Vol 20, p 708; *ibid.*, 1953, Vol 23, pp 1471, 1867; *ibid.*, 1954, Vol 24, p 803; *ibid.*, 1956, Vol 26, pp 407, 1926, 3319; *ibid.*, 1957, Vol 27, pp 365, 1805, 2076; *ibid.*, 1958, Vol 28, p 1999; *ibid.*, 1959, Vol 29, pp 1153, 1878, 2278, 2281, 2830, 3738, 3999; DAN SSSR, 1953, Vol 90, p 561; *ibid.*, 1954, Vol 95, p 285; *ibid.*, 1958, Vol 119, p 292; NDVSh, 1958, Vol 1, p 335) and on the chloroarylation of vinylacetylene and vinyl ethylacetylene (ZhOKh, 1959, Vol 29, p 2101), the authors investigated the addition of organolithium

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CIA-RDP86-00513R000824710005-4

compounds to the above hydrocarbons. Preliminary study (DAN SSSR, 1959, Vol 125, p 1041) showed that ethyllithium and butyllithium added easily at room temperature to these hydrocarbons and formed adducts, which on hydrolysis gave disubstituted propadienes and a residue with higher bp, containing ethylenes; at temperatures below -30° C, however, only propadienes were obtained. The present study deals with the addition of primary, secondary, and tertiary-alkylolithium compounds $[Li-C_2H_5; Li-C_3H_7; Li-C_4H_9; Li-CH_2-CH(CH_3)_2; Li-CH(CH_3)_2; Li-C(CH_3)_3]$ to vinylmethyl- and vinyl ethylacetylene, and establishes a new method for synthesizing disubstituted allenes. Alkylolithium ether solutions (in 0.9-1.0N concentration) were added to ether solutions of the starting hydrocarbons in a 1:1 ratio. The reaction was completed in 1 to 1.5 hr. Some experimental data are given in Table 2; 9 new disubstituted allenes are listed in Table 1. The

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structure of the adducts and the character of their bonds was confirmed by IR spectra, and also by the catalytic hydrogenation and subsequent identification of the saturated hydrocarbons obtained. There are 4 tables; 1 figure; and 9 references, 2 U.S., 7 Soviet. The U.S. references are: P. D. Bartlett, S. Fridman, M. Stibes, J. Am. Chem. Soc., 75, 1771 (1953); R. A. Jacobson, W. H. Carothers, *ibid.*, 55, 1624 (1933).

ASSOCIATION: Leningrad Institute of Technology (Leningradskiy tekhnologicheskii institut imeni Lensovet)

SUBMITTED: December 23, 1958

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Table 1

Compound	B.p. (pressure in mm.)	d_4^{20}	n_D^{20}	Mn _r	
				found	calculated
$\text{CH}_2=\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (I)	52-53° (150)	0.7273	1.4360	31.57	33.59
$\text{CH}_2=\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (II)	64-65 (40)	0.7555	1.4451	43.79	42.83
$\text{CH}_2=\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)_2$ (III)	62-63 (40)	0.7525	1.4450	43.03	42.83
$\text{CH}_2=\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{C}(\text{CH}_3)_3$ (IV)	52-53 (40)	0.7452	1.4418	41.08	42.83
$\text{CH}_2=\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (V)	77.5-78.5 (150)	0.7443	1.4432	39.26	38.21
$\text{CH}_2=\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (VI)	67-68 (40)	0.7512	1.4458	43.90	42.83
$\text{CH}_2=\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)_2$ (VII)	60-60.5 (40)	0.7488	1.4430	43.98	42.83
$\text{CH}_2=\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ (VIII)	82.5-83.5 (40)	0.7655	1.4498	48.51	47.45
$\text{CH}_2=\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{C}(\text{CH}_3)_3$ (IX)	70-70.5 (40)	0.7555	1.4458	48.78	47.45

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Table 2

Starting hydrocarbon	n_D^{20} LIR	Solvent	Temperature	Yield of allene (%)	Residue (g)
$\text{CH}_3\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$	C_2H_5	Petroleum ether	29°	16.2	10
	C_2H_5	Ethyl ether	-40	72	—
	$n\text{-C}_4\text{H}_{10}$	Petroleum ether	40	16.1	8.5
	iso- C_4H_{10}	Ethyl ether	-40	58	—
	tert- C_4H_{10}	Ethyl ether	-40	50.6	—
$\text{C}_2\text{H}_5-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$	C_2H_5	Petroleum ether	40	27.3	5
	C_2H_5	Ethyl ether	10	36.4	10
	$n\text{-C}_3\text{H}_7$	Ethyl ether	-10	74.2	—
	iso- C_3H_7	Ethyl ether	-40	80.5	—
	$n\text{-C}_4\text{H}_{10}$	Ethyl ether	30	16.0	5
	tert- C_4H_{10}	Petroleum ether	-40	52.2	—
		Ethyl ether			

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5.3610

78282

SOV/79-30-3-36/69

AUTHORS: Kormer, V. A., Petrov, A. A.

TITLE: Investigation of Conjugated Systems. CXVI.
Addition of Lithium Dialkylamides to Vinylacetylene
Hydrocarbons

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 3, pp
918-927 (USSR)

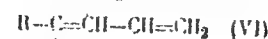
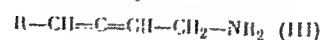
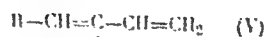
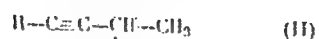
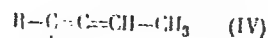
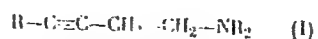
ABSTRACT: The course of addition of lithium dialkylamides
prepared from dimethyl-, diethyl-, dibutylamines,
and piperidine to vinylacetylenes (vinylacetylene,
vinylmethylacetylene, vinylethylacetylene, and
vinylbutylacetylene) was studied. The formation
of the following six amines with three types of
multiple bonds could be expected:

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Investigation of Conjugated Systems. CXVI

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where R=H or allyl. In the case of vinylacetylene, the reaction products, when treated with water, yield two types of acetylenic amines: $HC\equiv C-CH_2-CH_2NR_2$ and in small yield, $HC\equiv C-CH_2-\underset{\substack{| \\ CH_2NR_2}}{CH}-C\equiv CH$,

probably. The reaction of lithium dialkylamides with vinylmethacetylene yields primarily a dimer

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and polymers. The structure of amines depends on the nature of lithium dialkylamides; in the case of lithium dibutylamide, allenamine was formed primarily, and in all other, only acetylenamines $\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2\text{CH}_2\text{NR}_2$. The addition of lithium dialkylamides to vinyl- and vinylbutylacetylenes results in allenamines, $\text{R}-\text{CH}=\text{C}=\text{CH}-\text{CH}_2\text{NR}_2$ and small amounts of dimers and polymers. The prepared compounds are listed in Table 1. The yield of amines, dimers and polymers are given in Table 2. Allenamines are formed, evidently, as a result of 1,4-addition, and acetylenamines, either as a result of 1,2-addition, or by rearrangement of allene adducts in the course of the reaction into acetylene adducts (A. Ye. Favorskiy rearrangement). The structure of the prepared amines was proved by their infrared spectra, comparison to literature data, and by reduction to corresponding saturated amines followed by parallel synthesis of the latter. There are 3 figures; 3

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Table 1.

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(1)	(2)	γ_d^{20}	γ_D^{20}	n_D^{20}	
				(3)	(4)
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2\text{N}(\text{CH}_3)_2$	107° (758)	0.7892	1.4290	31.74	31.85
	107 (760)	0.7896	1.4290		
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	143-143.5 (765)	0.8031	1.4388	40.99	41.08
	85 (110)				
	85 (110)		1.4390		
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2\text{N}(\text{C}_4\text{H}_9)_2^a$	104-106 (20)	0.8098	1.4442	59.50	58.55
	80 (20)	0.8837	1.4740	43.64	43.50
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	60-61.5 (20)	0.7901	1.4378	46.24	45.70
	76 (40)				
	76 (40)		1.4380		
	90 (20)	0.8764	1.4712	48.25	48.12
$\text{C}_2\text{H}_5-\text{CH}=\text{C}=\text{CH}-\text{CH}_2\text{N}(\text{CH}_3)_2$	59-60 (20)	0.7964	1.4510	42.33	42.15
$\text{C}_2\text{H}_5-\text{CH}=\text{C}=\text{CH}-\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	85-86 (20)	0.8111	1.4554	51.30	51.39
$\text{C}_2\text{H}_5-\text{CH}=\text{C}=\text{CH}-\text{CH}_2\text{N}(\text{C}_4\text{H}_9)_2$	136-136.5 (20)	0.8150	1.4558	69.80	69.86
$\text{C}_2\text{H}_5-\text{CH}=\text{C}=\text{CH}-\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3$	113-114 (20)	0.8900	1.4800	53.35	52.99
$\text{C}_4\text{H}_9-\text{CH}=\text{C}=\text{CH}-\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$	114-115 (20)	0.8148	1.4570	60.16	60.62

Key to Table 1: (1) Compound; (2) bp (pressure in mm); (3) Found; (4) Calculated.

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Table 2.

(1)	(2)	(3)	(4)	(5)
$\text{HC}\equiv\text{C}-\text{CH}=\text{CH}_2$	$\text{Li}-\text{N}(\text{CH}_3)_2$	24	25	} (6)
	$\text{Li}-\text{N}(\text{C}_2\text{H}_5)_2$	24	20	
	$\text{Li}-\text{N}(\text{C}_4\text{H}_9)_2$	24	10	
	$\text{Li}-\text{N}(\text{CH}_2)_3$	3	30	
$\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$	$\text{Li}-\text{N}(\text{C}_2\text{H}_5)_2$	24	5	60
	$\text{Li}-\text{N}(\text{C}_4\text{H}_9)_2$	1.5	4	50
	$\text{Li}-\text{N}(\text{CH}_2)_3$	1.5	9	56
$\text{C}_2\text{H}_5-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$	$\text{Li}-\text{N}(\text{CH}_3)_2$	1.0	40	10
	$\text{Li}-\text{N}(\text{C}_2\text{H}_5)_2$	1.5	45	10
	$\text{Li}-\text{N}(\text{C}_4\text{H}_9)_2$	1.5	55	} (7)
	$\text{Li}-\text{N}(\text{CH}_2)_3$	1.5	50	
	$\text{Li}-\text{N}(\text{CH}_2)_4\text{O}$	24	10	
$\text{C}_4\text{H}_9-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$	$\text{Li}-\text{N}(\text{C}_2\text{H}_5)_2$	1.5	40	5

Key to Table 2: (1) Starting hydrocarbon; (2) lithium dialkylamide; (3) Reaction time (hours); (4) Yield (%); (5) Yield of dimers and polymers (in %); (6) None; (7) Was not determined.

Card 5/6

Investigation of Conjugated Systems

APPROVED FOR RELEASE: 06/14/2000

CIA-RDP86-00513R000824710005-4

SOV/79-30-3-36/69

tables; and 16 references, 8 Soviet, 4 U.S., 2 German, 2 French. The U.S. references are: Gilman, H., J. Am. Chem. Soc., 67, 2106 (1945); Urner, R. S., Bergstrom, F. W., J. Am. Chem. Soc., 67, 2110 (1946); Hammel, M., Levine, R., J. Org. Chem., 15, 162 (1950); Engelhardt, V. A., J. Am. Chem. Soc., 78, 107 (1956).

ASSOCIATION:

Lensovet Leningrad Technology Institute (Leningradskiy tekhnologicheskii institut imeni Lensoveta)

SUBMITTED:

April 22, 1959

Card 6/6

5.3630

78513
S07/79-30-3-67/69

AUTHORS: Petrov, A. A., Kormer, V. A.

TITLE: Letters to the Editor. Concerning Addition of Lithium Phosphides to Vinylacetylenes

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 3, p 1056 (USSR)

ABSTRACT: The authors report that lithium alkyl phosphides readily add (even in the cold) to vinylacetylenes. 1-Diethylphosphinylohexa-2,3-diene (I) was obtained by treating an ether solution of the products of reaction between lithium diethylphosphide and vinylacetylene with water. I has bp 78-79° (5 mm), d_4^{20} 0.8569, n_D^{20} 1.5025.

I has a characteristic phosphine odor, fumes on exposure to the air (all work with I was conducted in an argon atmosphere). The authors consider the above reaction to be a new method for preparing unsaturated alkylphosphines from unsaturated hydrocarbons. There is 1 Soviet reference.

Card 1/2

Letters to the Editor. Concerning Addition
of Lithium Phosphides to Vinylacetylenes

78313
SOV/79-30-3-67/69

ASSOCIATION: Lensovet Leningrad Institute of Technology (Leningradskiy
tekhnologicheskiiy institut imeni Lensoveta)

SUBMITTED: November 19, 1959

Card 2/2

S/079/60/030/05/16/074
B005/B126

AUTHORS: Chelpanova, L. F., Kormer, V. A., Nemirovskiy, V. D.
TITLE: Synthesis and Rearrangement of α -Glycols of the Ethylene
Series. VIII. Rearrangement of 2,3-Dimethylpentene(4)-
diol(2,3) 7

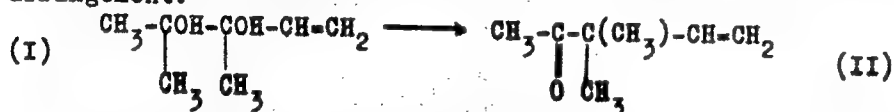
PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 5, pp. 1476-1479

TEXT: With 2,3-dimethylpentene(4)-diol(2,3) as an example, A. Ye. Favorskiy and his students showed that unsaturated α -glycols in the presence of strong sulfuric acid can be the cause of a rearrangement of pinacolin. The authors examined the behavior of the similarly formed α -glycol of the ethylene series (2,3-dimethylpentene(4)-diol(2,3)) (I) on being heated with diluted sulfuric acid. When the compound (I) is heated to 60-70° with 10% sulfuric acid, a bright yellow substance separates from the acid solution, with a boiling range (at 4 mm pressure) of 107-110°. This compound has the gross formula $C_7H_{12}O$, contains no hydroxyl group, discolors aqueous solutions of potassium permanganate and

Card 1/3

Synthesis and Rearrangement of α -Glycols of the Ethylene Series. VIII. Rearrangement of 2,3-Dimethylpentene(4)-diol(2,3) S/079/60/030/05/16/074 B005/B126

bromine and gives a positive iodoform reaction. The substance forms a 2,4-dinitrophenyl-hydrazone with a melting point of 85-87°C. The formation of this unsaturated ketone can be explained by pinacolin rearrangement:



The analysis of the infrared spectrum of the compound (II) proves the given structure. The infrared spectra were taken with a type MKC-14 (IKS-14) spectrophotometer. The initial product (I), which is not described in publications, was synthesized by hydrogenation of the acetylene glycols (Ref. 1). Apart from the unsaturated ketone (II), another product formed by the action of H_2SO_4 on (I), with a boiling range (at a pressure of 4 torr) of 120-122°C; its structure could not be determined. The synthesis of the initial product (I), starting with dimethylacetylenylcarbinol, is described in the experimental part. The reaction with sulfuric acid is also described. The boiling point,

Card 2/3

S/079/60/030/007/030/039/XX
B001/B066

AUTHORS: Petrov, A. A., Kormer, V. A., and Yakovleva, T. V.

TITLE: Investigations in the Field of Conjugate Systems. CXX. Addition of Lithium Alkyls to Vinyl Isopropenyl Acetylene 1

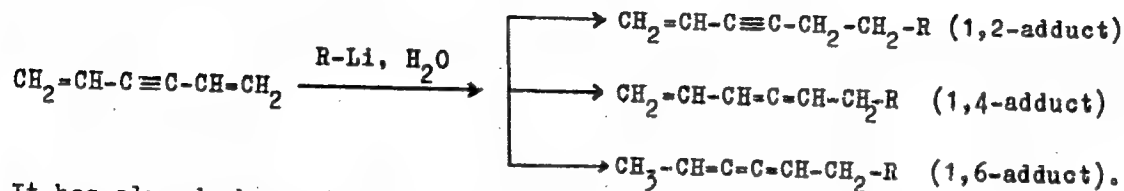
PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2238-2243

TEXT: The authors stated in Ref. 1 that lithium alkyls readily add to vinyl alkyl acetylenes, and that symmetrically bisubstituted allenes (1,4-bond) are formed after treating the reaction mass with water. Telomerization does not take place at low temperatures. It was of interest to determine the mode of addition of lithium alkyls to hydrocarbons with a longer chain of conjugate multiple bonds, in particular to diene hydrocarbons. Here, the formation of 1,2-, 1,4-, and 1,6 adducts was to be expected since the addition to the central carbon atoms of the conjugate system seems unlikely and has not been observed as yet (Ref. 2):

Card 1/3

Investigations in the Field of Conjugate
Systems.CXX. Addition of Lithium Alkyls to
Vinyl Isopropenyl Acetylene

S/079/60/030/007/030/039/XX
B001/B066



It has already been shown that the addition of lithium alkyls to divinyl acetylene takes place in the 1,4-position to give vinyl allene hydrocarbons (Ref. 3). The structures of the latter were confirmed by their infrared spectra (absorption bands of the vinyl group and of the allene system without those of the acetylene group), and by exhaustive hydrogenation. In the present paper, the addition of lithium to vinyl isopropenyl acetylene was studied. Due to its unsymmetrical structure, the addition may take place in this case to the vinyl or isopropenyl group to give compounds (I) and (II). On the strength of the considerations of Refs. 4 and 5, the addition of radicals to the vinyl group had to be expected as this group had lost electrons. The same mode of addition was predicted owing to the radical character of the reaction course, since radical processes are

Card 2/3

85611

53600

2209, 1153

S/079/60/030/007/031/039/XX
B001/B066

AUTHORS: Petrov, A. A., Kormer, V. A., and Stadnichuk, M. D.
TITLE: Investigations in the Field of Conjugate Systems. CXXI.
Addition of Lithium Alkyls to Trialkylvinyl Acetylenyl
Silane η

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7, pp. 2243-2248

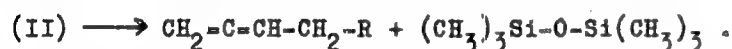
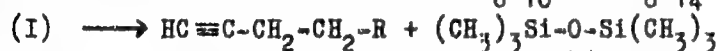
TEXT: The authors continued their investigation of the reaction of lithium alkyls with compounds having a double and a triple bond, and studied, taking into account the papers of Refs. 3, 4, the addition of lithium ethyl, propyl, isopropyl, butyl, and tertiary butyl to trimethylvinyl acetylenyl silane. By treating the reaction product with water they obtained the addition products of the expected composition: $(CH_3)_3Si - C_4H_4 - R$. According to the mode of addition of lithium alkyls, structures (I) to (VI) were possible. In the infrared spectra of all adducts, frequencies of the stretching vibrations of a triple and allene bond system were found. In the spectral region which is characteristic of the stretching vibrations of the double bonds, no absorption was observable (Diagram 1). These
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85611

Investigations in the Field of Conjugate
Systems. CXXI. Addition of Lithium Alkyls
to Trialkylvinyl Acetylenyl Silane

S/079/60/030/007/031/039/XX
B001/B066

data show that the adducts are mixtures of acetylene and allene compounds, and that formulas (IV) and (VI) are negligible. On hydrogenation of the silicon hydrocarbons obtained from the adducts with lithium ethyl and lithium butyl by means of PdCaCO_3 , trimethylhexyl and trimethyloctyl silanes were obtained accordingly. Their structure was confirmed by comparing their infrared spectra with those of authentic samples of silicon hydrocarbons (Diagram 2). Thus all formulas, except (I) and (II), may be excluded. The ratio between the acetylene and allene isomers was found from their hydrolysis. The hydrolytic cleavage of two silicon hydrocarbons, with $\text{R} = \text{C}_2\text{H}_5$ and C_4H_9 , gave hexamethyl disiloxane and mixtures of acetylene-allene hydrocarbons, C_6H_{10} and C_8H_{14} , according to the scheme



Since hydrolysis took place at $65-70^\circ$, allene-acetylene isomerization was impossible in this case. The acetylene isomer content in the mixture was determined analytically (Ref. 5). Also the difference between the

Card 2/3

S/079/60/030/010/015/030
B001/B066

AUTHORS: Bal'yan, Kh. V., Petrov, A. A., Borovikova, N. A.,
Korner, V. A. and Yakovleva, T. V.

TITLE: Hydrogenation of Unsaturated Compounds in the Presence of
Colloidal Palladium. XIV. Some Peculiarities of the
Hydrogenation of Bisubstituted Allene Hydrocarbons

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 10,
pp. 3247 - 3253

TEXT: There are only few data available in publications concerning special cases of the hydrogenation of seven bisubstituted allenes (Table). In the present paper, the authors study some rules governing the hydrogenation of the following bisubstituted allene hydrocarbons: octadiene-3,4; nonadiene-3,4; decadiene-3,4; 7-methyl octadiene-2,3; 7-methyl octadiene-3,4; 6,6-dimethyl heptadiene-2,3; and 7,7-dimethyl octadiene-3,4. It was found that the first hydrogen mole is usually added at an increasing rate, after which hydrogenation slows down considerably (Diagram 1). In hydrocarbons of isostructure this rule

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Hydrogenation of Unsaturated Compounds in the Presence of Colloidal Palladium. XIV. Some Peculiarities of the Hydrogenation of Bisubstituted Allene Hydrocarbons S/079/60/030/010/015/030 B001/B066

manifests itself still more distinctly. The hydrogenation of allenes takes place selectively, and, when taking up half of the calculated hydrogen quantity, a mixture of olefins with a double bond in position 2-, 3-, or 4- is formed. Allene hydrocarbon reacts completely in this case. Alkenyl allenes (octatriene-1,3,4; decatatriene-1,3,4; 2-methyl octatriene-1,3,4; 8-methyl nonatriene-1,3,4) are hydrogenated in the same way: After taking up about 2 moles of hydrogen, the reaction rate decreases rapidly. Allenes and hydrocarbons having a double bond in the end position disappear completely or to a considerable extent after taking up the first hydrogen mole. The infrared spectra of the hydrogenation products of allenes with 50% of the hydrogen quantity are not indicative of allene compounds (Diagram 2). Diagram 1 does not show any characteristic differences of the hydrogenation rates of 2,3- and 3,6-dienes. Diagram 3 shows curves for the hydrogenation rates of alkenyl allenes; Diagram 4 shows the infrared spectra of the hydrogenation products of alkenyl allenes in a hydrocarbon/hydrogen ratio of 1:1.

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APPROVED FOR RELEASE: 06/14/2000

CIA-RDP86-00513R000824710005-4

Hydrogenation of Unsaturated Compounds in the Presence of Colloidal Palladium. XIV. Some Peculiarities of the Hydrogenation of Bisubstituted Allene Hydrocarbons S/079/60/030/010/015/030 B001/B066

The investigation results thus indicate that the hydrogenation of bisubstituted allenes takes place selectively, and is similar to the hydrogenation of acetylenes having the acetylene group in the end position. In the case of alkenyl allenes, the direction of hydrogenation depends to a certain extent on the hydrocarbon structure. There are 4 figures, 2 tables, and 9 Soviet references.

ASSOCIATION: Leningradskiy tekhnologicheskii institut im. Lensovet (Leningrad Technological Institute imeni Lensovet)

SUBMITTED: October 25, 1959

Card 3/3

86511

53700

2209, 1273, 1274

S/079/60/030/011/023/026
B001/B055

AUTHORS: Petrov, A. A., Kormer, V. A., and Savich, I. G.

TITLE: On the Mechanism of Lithium-alkyl Addition to Alkynes

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 11, pp. 3845-3846

TEXT: By treating the reaction product obtained from addition of lithium alkyls to alkynes with water, one obtains allenes (Ref. 1). In order to explain the reaction mechanism, the authors studied the IR spectra of solutions of lithium butyl and vinyl-ethyl acetylene in undecane and a mixture of undecane and ether (1 : 1). The reaction was slow in the former solvent, and after the reaction mixture was kept at 20°C for 24 h, the deformation frequency of vinyl-ethyl acetylene was still visible in the spectrum. In the presence of ether, however, the reaction is complete in a few minutes, with occurrence of spontaneous heating. Immediately after mixing the components, the spectrum, besides containing the frequencies of butyl lithium (Refs. 2 and 3) and vinyl acetylene, shows a gradually intensifying marked frequency at 1865 cm^{-1} , which probably corresponds to the

Card 1/3

86511

On the Mechanism of Lithium-alkyl Addition
to Alkynes

S/079/60/030/011/023/026
B001/B055

associated molecule $C_2H_5-CLi-C=CH-CH_2-C_4H_9$ (I). After leaving the mixture to stand for 12 h, a high frequency at 1780 cm^{-1} appears in the spectrum. On treating the reaction mixture with water, these frequencies disappear from all the spectra taken at the various stages of the reaction, accompanied by the appearance of the allene-group frequency and the deformation frequency at 1865 cm^{-1} (Ref. 5). That this frequency pertains to the vibrations of the associated allene - lithium complex (I) is confirmed by the fact that this frequency at 1865 cm^{-1} and also the frequency at 1780 cm^{-1} gradually appear in the spectrum of the undecane solution of butyl lithium and ethyl-butyl allene. On treatment of these solutions with water, ethyl-butyl allene was regenerated, and treatment with CO_2 gave propadiene carboxylic acid, indicating a metallation reaction. On the other hand, enynes which do not form allenes by reaction with lithium alkyls, form complexes which apparently absorb at 2050 cm^{-1} and not at 1865 cm^{-1} . It is concluded from the data given in this paper, that the addition of lithium alkyls to vinyl-alkyl acetylenes proceeds via lithium allenes as inter-

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86511

On the Mechanism of Lithium-alkyl Addition
to Alkenynes

S/079/60/030/011/023/026
B001/B055

mediates. The allene configuration is therefore formed when lithium alkyl adds to the conjugated system, and not when the reaction mixture is treated with water. There are 5 Soviet references.

ASSOCIATION: Leningradskiy tekhnologicheskii institut imeni Lensovet
(Leningrad Institute of Technology imeni Lensovet)

SUBMITTED: July 28, 1960

Card 3/3

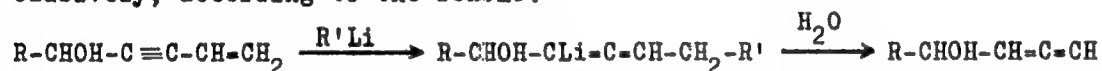
S/079/60/030/012/006/027
B001/B064

AUTHORS: Kormer, V. A. and Petrov, A. A.

TITLE: Studies in the Field of the Conjugate Systems. CXXVI.
Addition of Lithium Alkyls to Vinyl Acetylene Alcohols

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 12,
pp. 3890-3894

TEXT: In continuation of previous papers (Refs. 1, 2) the authors investigated the order of addition of lithium alkyls to the vinyl-alkyl acetylene derivatives, especially to vinyl acetylene alcohols. The secondary and tertiary vinyl acetylene alcohols, methyl- and dimethyl-vinyl acetylene carbinol were studied. The reaction proceeded under cooling in ether, the demethylation with water. Thus, allene alcohols formed almost exclusively, according to the scheme:



$\text{-CH}_2\text{-R'}$. The structure of carbon skeleton in these alcohols was proven by hydrogenation into the respective saturated compounds. Hydrogenation of the Card 1/2

Studies in the Field of the Conjugate Systems. S/079/60/030/012/006/027
CXXVI. Addition of Lithium Alkyls to Vinyl B001/B064
Acetylene Alcohols

alcohol obtained from the adduct of lithium butyl to methyl-vinyl acetylene carbinol yielded decanol-2 which was identified by the decanol obtained from magnesium octyl bromide and acetaldehyde. 2-methyl decanol-2 whose constants and IR spectra do almost correspond to the decanol obtained from magnesium octyl bromide and acetone, was obtained by hydrogenating tertiary alcohol resulting from the addition product of lithium butyl to dimethyl-vinyl acetylene carbinol. Thus, the radical was found to add in both cases to the terminal carbon atom of the conjugate system. The problem of the arrangement of the multiple bonds and their nature was clearly solved by means of the infrared spectra of the unsaturated alcohols (Diagrams 1, 2). These data show that the addition of the lithium alkyls to vinyl acetylene alcohols proceeds in the same way as that to vinyl-alkyl acetylenes and yields almost exclusively allene alcohols (with a small amount of acetylene- and 1,3-diene alcohols). There are 2 figures and 6 references: 5 Soviet and 1 German.

ASSOCIATION: Leningradskiy tekhnologicheskii institut imeni Lensovet
(Leningrad Technological Institute imeni Lensovet)

SUBMITTED: January 21, 1960
Card 2/2

81704
S/020/60/132/05/34/069
B011/B126

5.3630(A)

AUTHORS: Petrov, A. A., Korner, V. A.

TITLE: The Addition of Lithium-alkyl Phosphides to Vinyl-
acetylene¹Hydrocarbons

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 5,
pp. 1095 - 1098

TEXT: The authors have previously (Ref. 1) established that lithium-dialkyl-amides are added to vinyl-acetylene-hydrocarbons, and that allene- or acetylene-amines are formed after the adduct has been treated with water. The authors wanted to study the behavior of other compounds of the type $R_2E - Li$ under the same conditions (E - an element of the V. group of the periodic system). To do this they analyzed the reaction of vinyl-acetylene and two of its homologs: vinylmethyl- and vinyl-ethylacetylene, with lithiumdiethyl- and lithiumdibutylphosphides. As expected, the addition of lithiumphosphides took place in all three possible ways (I), (II), and (III). On the other hand, in the case of

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The Addition of Lithium-alkyl Phosphides to
Vinyl-acetylene Hydrocarbons

81704
S/020/60/132/05/34/069
B011/B126

vinylmethyl- and vinylethyl-acetylene, tertiary allene-phosphines (II) formed almost without exception. Tertiary phosphine, which formed by treatment of the adduct of lithiumdibutylphosphide on vinylacetylene, undoubtedly contained 1-dibutylphosphinobutene-3, according to the spectral data. Some 40% acetylene was found in it by the usual method. Vinylmethyl- and vinylethylacetylene behave in the same way in the reaction with lithium phosphides, while vinylethylacetylene gives allene products, and vinylmethylacetylene gives mainly the dimer and polymers, on the reaction with lithiumalkylamides. Considerable quantities of high-boiling phosphorus-containing products are also formed in all cases, as well as tertiary phosphines. The authors suppose that they are higher telomers of the phosphines isolated from them. Lithiumdi-alkylphosphides react easily with halogen derivatives, producing saturated tertiary phosphines. The authors obtained diethylbutylphosphine from the action of lithiumdiethylphosphide on butylchloride. Tributylphosphine formed in a similar way from lithiumdibutylphosphide and butylchloride. No alkylchloride remained from the reaction on the production of lithiumalkyls. The phosphines with an allene group are described here for the first time. The tertiary allene-phosphines

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Card 2/3

BAL'YAN, Kh.V.; PETROV, A.A.; BOROVIKOVA, N.A.; KORMER, V.A.; YAKOVLEVA, T.V.

Hydrogenation of unsaturated compounds in the presence of colloidal palladium. Part 14: Some characteristics of the hydrogenation of disubstituted allene hydrocarbons. Zhur.ob.khim. 30 no.10:3247-3253 0 '61. (MIRA 14:4)

1. Leningradskiy tekhnologicheskii institut im. Lensoвета.
(Hydrogenation) (Olefins)

20947

S/079/61/031/004/001/006
B118/B208

5 3760

2209, 1164, 1279

AUTHORS: Petrov, A.A., Kormer, V.A., and Stadnichuk, M.D.

TITLE: Studies in the field of conjugate systems. CXXXIII.
Addition of lithium dialkyl amides to trialkyl-silyl-
buten-3-yne (Enyne compounds. LII)

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 4, 1961, 1135 - 1139

TEXT: As was previously shown, lithium dialkyl amides readily add to vinyl acetylene hydrocarbons to form acetylene or allene amines, depending on the structure of vinyl acetylene hydrocarbons. Considering the considerable dependency of the reaction direction on the structure it was of interest to study more thoroughly the reactions of lithium dialkyl amides with enyne compounds. The present paper describes the reactions of lithium diethyl amide and lithium piperidide with 1-trimethyl-silyl-buten-3-yne-1. The latter adds lithium dialkyl amides even in the cold, but the adduct is more or less cleft when treated with water, forming the amine and hexamethyl siloxane owing to the weak hydrolytic stability of the C—Si—bond in α -position to the multiple bond. Reaction of 1-trimethyl-silyl-

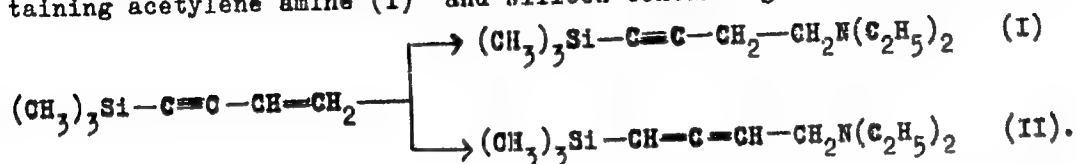
Card 1/4

20947

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B118/B208

Studies in the field of ...

-buten-3-yne-1 with lithium diethyl amide gives a mixture of silicon-containing acetylene amine (I) and silicon-containing allene amine (II):



The infrared spectrum of this mixture shows a very intense frequency of stretching vibrations of the acetylene bond (2171 cm^{-1}) and an intense band of stretching vibrations of the allene grouping (1937 cm^{-1}). In the range 1600 cm^{-1} no absorption was observed which indicated the absence of an isomer with a conjugate system of double bonds. The presence of silicon is confirmed by the characteristic frequencies 1208 and 1256 cm^{-1} , that of the $(\text{CH}_3)_3\text{Si}$ grouping by the frequencies 843 and 762 cm^{-1} . Heating with 10% KOH solution in methanol results in a cleavage of the mixture to form hexa-

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S/079/61/031/004/001/006
B118/B208

Studies in the field of ...

methyl siloxane and a mixture of acetylene and allene amines. The structure of the amines present in the mixture was confirmed spectroscopically and chemically. Reaction of trimethyl-silyl-butyne with lithium piperide gave a mixture of silicon-free amines with silicon-containing amines. The former product consisted of nearly pure 1-piperidino-butyne-3. Analysis gave 90% of a compound with an acetylene group in end position whose infrared spectrum rather corresponded to that of 1-piperidino-butyne-3. The second product is an adduct of piperidine to trimethyl-silyl-buten-3-yne-1 and, with respect to structure, also an acetylene compound. It was thus confirmed that, contrary to vinyl acetylenes, the 1-trimethyl-silyl-buten-3-yne-1 tends to form acetylene compounds in reactions with lithium dialkyl amides. The mode of addition depends on the nature of the amine. The formation of silicon-free compounds seems to be due to the instability of the C—Si—bond to bases. The two resultant silicon-containing amines are colorless oils completely soluble in dilute hydrochloric acid. If they are separated from this solution, they are, however, partially cleft at the C—Si—bond. There are 1 figure and 6 references: 5 Soviet-bloc and 1 non-Soviet-bloc. The reference to the English language-publication reads as follows: E.L. Warrisk, J.Am.Chem.Soc., 68, 2455, (1946).

Card 3/4

20947

S/079/61/031/004/001/006
B118/B208

Studies in the field of ...

ASSOCIATION: Leningradskiy tekhnologicheskii institut imeni Lensovet.
(Leningrad Technological Institute imeni Lensovet)

SUBMITTED: April 29, 1960

Card 4/4

PETROV, A.A.; PORFIR'YEVA, Yu.I.; KORMER, V.A.,

Conjugated systems. Part 135: Course of the addition of alkyl-
hypobromites and lithium-alkyls to vinylpropenylacetylene. Zhur.ob.
khim. 31 no.5:1518-1524 My '61. (MIRA 14:5)

1. Leningradskiy tekhnologicheskii institut imeni Lenooveta.
(Hypobromites) (Lithium organic compounds) (Heptadienyne)

33934

S/079/62/032/001/012/016
D204/D302

// 2232

// 2223

AUTHORS: Kormer, V.A., Petrov, A.A., Savich, I.G., and
Podporina, T.V.

TITLE: The kinetics and mechanism of the addition of lithium
butyl to vinyl ethyl acetylene

PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 1, 1962, 318-319

TEXT: LiBu was reacted with vinyl ethyl acetylene (I) in undecane
at 20 and 30°C, under argon, in molar proportions of 1 : 1 and 1 :
2. At 20°C the reaction gave an allene hydrocarbon (II) in 56 %
yield after 20 hours. Concentrations of I and II were determined by
infrared spectroscopy. The reaction proved to be kinetically of the
first order, with velocity constants $K_{20}^0 = 0.0643$, $K_{30}^0 = 0.1333$ ✓

hr^{-1} and with an energy of activation equal to 12.7 Kcal/mole. The
rate controlling process is thought to be the monomolecular decom-
position of a complex which forms as an intermediate stage. It was
also observed that I decomposes faster than II is formed, especial-
ly at the higher temperature and when I was in excess. This is as-

Card 1/2

The kinetics and mechanism of ...

S/079/62/032/001/012/016
D204/D302

cribed to side processes. There are 3 Soviet-bloc references.

ASSOCIATION: Leningradskiy tekhnologicheskii institut imeni Lenso-
veta (Leningrad Institute of Technology im. Lensovet)

SUBMITTED: September 2, 1961

KORMER, V.A.; PETROV, A.A.

Addition of diisobutyl aluminum hydride and triisobutylaluminum
to vinylacetylene. Dokl. AN SSSR 146 no.6:1343-1346 0 '62.
(MIRA 15:10)

1. Leningradskiy tekhnologicheskii institut im. Lensoveta.
Predstavleno akademikom B.A. Arbuzovym.
(Aluminum compounds) (Butenyne)

36080
S/079/62/032/004/007/010
D287/D301

11/750
15.8150
AUTHOR: Petrov, A.A., Zavgorodniy, V.S., and Kormer, V.A.
TITLE: Dialkylboron and dialkylaluminum vinylacetylene
PERIODICAL: Zhurnal obshchey khimii, v. 32, no. 4, 1962, 1349-1350
TEXT: The present work is a continuation of earlier investigations by the authors on the character of bonds with acetylene and vinyl-acetylene groups and on the position of these bonds. Dibutylboron iso-propenylacetylene, prepared in a current of nitrogen in ether, had after high-vacuum distillation a boiling point of 22 - 25°C at 0.1 mm pressure, $n_D^{20} = 1.4509$; the substance was instantaneously inflammable on air. The 2145 cm^{-1} band in the IR spectrum was assigned to treble bond substances, the 1609 cm^{-1} band to double bond substances, the 900 cm^{-1} band to the deformation vibrations of the iso-propenyl group. The boron atom, therefore, lowers the frequency of the valency vibrations of the treble bond to the same extent as the Si atom, but has only a negligible effect on the frequency of the double bond valency vibrations. The dialkylaluminum vinylacetylenes
Card 1/2

APPROVED FOR RELEASE: 06/14/2000

CIA-RDP86-00513R000824710005-

S/079/62/032/004/007/010
D287/D301

Dialkylboron and dialkylaluminum ...

were synthesized in an argon current. Both compounds were oils, subject to spontaneous combustion on air, with a characteristic 2075 cm^{-1} IR absorption band. The compounds polymerize during storage or heating, forming allene adducts by 1,4-addition; their characteristic IR absorption band is at $\sim 1920 \text{ cm}^{-1}$. Tri-iso-butyl aluminum and di-iso-butyl aluminum hydride also form alkyl aluminum vinyl acetylenes with vinyl acetylene, as well as treble bond adducts. Strong characteristic bands appear at 1530 and 2070 cm^{-1} in the IR spectrum. Frequency of the multiple bonds is shifted towards the usual values when the dialkyl compounds are treated with absolute ether; this also causes a sharp decrease in the intensity of the bands. There are 3 references: 2 Soviet-bloc and 1 non-Soviet-bloc.

ASSOCIATION: Leningradskiy tekhnologicheskii institut im. Lensovet
(Leningrad Institute for Technology im. Lensoviet)

SUBMITTED: April 15, 1962

Card 2/2

L 60198-65 ENT(m)/EPF(c)/EMP(j)/T Pe-4/Pr-4 GS/JAJ/RM

ACCESSION NR: AT5019601

UR/0000/54/000/000/0003/0013

AUTHOR: Karotkov, A. A.; Kormer, V. A.; Krupyshev, M. A.; Feringer, D. P.

TITLE: Synthesis of isoprene rubber

33
B+

ABSTRACT: Vsesoyuznyy nauchno-issledovatel'skiy inatitut sinteticheskogo kauchuka. Polimerizatsiya izoprena kompleksnymi katalizatorami (Polymerization of isoprene by complex catalysts). Moscow, Izd-vo Khimiya, 1964, 7-13

TOPIC TAGS: synthetic rubber, isoprene, polymerization, Ziegler catalyst, organo-metallic complex

ABSTRACT: Polymerization of isoprene was studied with Ziegler-type and organometallic- π -complex catalysts in order to simulate the natural rubber. Production of commercial synthetic SKI-3 rubber is based on the results of this study. In general, the Ziegler-type catalyst [TiCl_4 reduced with $\text{Al}(\text{C}_2\text{H}_5)_3$] gave isoprene polymers containing up to 95% of cis-1,4 units, while the organo- π -complexes of Li, Zn, and Al gave polymers with varying ratio of cis-1,4 to cis-3,4 and trans-1,4 units. The higher the cis-1,4 unit content in the polymer the better the mechanical properties of the vulcanized product. In the case of the Ziegler catalyst, the experiments

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L 60198-65

ACCESSION NR: AT5019601

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were conducted at -30° to 100°C using a 1:1 and 1:2 mixture of $TiCl_4$ and $(iso-C_4H_9)_3Al$ as catalyst. The initial isoprene concentration was 15-50 wt. %, the catalyst concentration was 2.2-3.6 wt. % based on monomer, and the polymerization duration was 1-2 hours. A mixture of isopentenes, isopropyl ethylene, pentene-1, trimethyl ethylene, and methylethyl ethylene were used as solvents. Preparation of the Ziegler catalysts prior to the polymerization experiment resulted in the highest (and best mechanical and physical properties of polymers (tensile strength and relative elongation). Polymers prepared at 50°C have the best mechanical properties. Unsaturated hydrocarbon solvents gave lower rates of isoprene polymerization than the saturated hydrocarbon solvents. The rate of polymerization reaction is reduced and the polymer quality is impaired when there is no solvent. List: 8 tables and 2 figures.

ASSOCIATION: none

SUBMITTED: 24Oct64

ENCL: 00

SUB CODE: MTJCC

NO REF SOV: 006

OTHER: 003

Card 2/2

PETROV, A. A.; KORMER, V. A.

Metalation and isomerization of vinylalkyl acetylenes by
the action of alkali metal amides in liquid ammonia. Zhur. ob.
Khim. 34 no.6:1868-1873 Je '64. (MIRA 17:7)

1. Leningradskiy tekhnologicheskii institut imeni Lensoвета.

STADNICHUK, T.V.; KORMER, V.A.; PETROV, A.A.

Action of lithium alkyls on vinylacetylene ethers and chlorides.
Zhur. ob. khim. 34 no.10:3279-3284 O '64.

Action of lithium dialkylamides on vinylacetylene ethers and chlorides. Ibid.:3284-3289

(MIRA 17:11)

1. Leningradskiy tekhnologicheskiy institut im. Lensoвета.

PEREPPEL'KIN, O.V.; KORMER, V.A.; BAL'YAN, Kh.V.; PETROV, A.A.

Allene-acetylene rearrangement in lithium allene oxidation.
Zhur. org. khim. 1 no.9:1705-1706 S '65.

(MIRA 18:12)

1. Leningradskiy tekhnologicheskii institut imeni Lensovata.
Submitted May 25, 1965.

L 3204-66 EWT(m)/EPF(c)/ENP(j)/T RM

ACCESSION NR: AP9016306

UR/0190/64/006/012/2202/2202

AUTHOR: Babitskiy, B. D.; Dogoplosk, B. A.; Kormer, V. A.; Lobach, M. I.; Tinyakova, Ye. I.; Chesnokova, N. N.; Yakovlev, V. A.

TITLE: Stereospecific polymerization of butadiene in the presence of pi-allylic complexes

SOURCE: Vysokomolekulyarnyye soyedineniya, v. 6, no. 12, 1964, 2202

TOPIC TAGS: polymerization, butadiene, catalysis, macromolecular chemistry

Abstract: It was shown that the polymerization of butadiene in benzene solutions under the influence of catalytic systems based on pi-allylic complexes of nickel and metal halides ($TiCl_4$, VCl_4 , WCl_6 , $AlBr_3$, and $NiCl_2$) leads to the formation of a polymer with predominantly (up to 94%) cis-1,4-units. The stereospecificity of these catalysts does not depend on the nature of the metal in the Lewis acid. The polymerization temperature was 20-50° and the time 8-15 hours.

ASSOCIATION: none

SUBMITTED: 13 Jul 64

NO REF SOV: 000

ENCL: 00
OTHER: 000

SUB CODE: 00, 00
JPRS

Card 1/1

BABITSKIY, B.D.; DOLGOPLOSK, B.A.; KORMER, V.A.; LOBACH, M.I.; TINYAKOVA, Ye.I.; YAKOVLEV, V.A.

Influence of the nature of halogen atom on the stereospecificity of π -allyl complexes of nickel in butadiene polymerization.

Izv. AN SSSR. Ser. khim. No.8:1507 '65.

(MJRA 18:9)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka im. S.V. Lebedeva i Institut neftekhimicheskogo sinteza im. A.V. Topchiyeva AN SSSR.

L 7648-66 EWT(m)/EPF(c)/EWP(j) UM
 ACC NR: AP5025036 SOURCE CODE: UR/0286/65/000/016/0084/0084
 AUTHORS: Babitskiy, B. D.; ⁴⁴Kormer, V. A.; ⁴⁴Lapuk, I. M.; ⁴⁴Lobach, M. I.; ⁴⁴Chesnokova, N. N. ⁴¹
 ORG: none ⁴⁴
 TITLE: Method for obtaining cis-1,4-polybutadiene rubber. ⁴⁴Class 39, No. 173948 ⁴¹
 /announced by All-Union Scientific Research Institute for Synthetic Rubber im.
 academician S. V. Lebedev (Vsesoyuznyy nauchno-issledovatel'skiy institut
 sinteticheskogo kauchuka) ⁴⁴
 SOURCE: Byulleten' izobreteniy i tovarnykh znakov, no. 16, 1965, 84
 TOPIC TAGS: rubber, butadiene, polymer, polybutadiene rubber, catalyst, *polymer-ization*
 ABSTRACT: This Author Certificate presents a method for obtaining cis-1,4-polybutadiene rubber by thermal polymerization of butadiene in the presence of a catalyst. The catalyst consists of tetranickelcarbonyl and metal-containing compounds. The metal-containing compounds used are transition metal salts of group V or VI soluble in hydrocarbons, for instance, vanadium tetrachloride, vanadium
 Card 1/2 UDC: 678.762.2
 2

L 7648-66

ACC NR: AP5025036

oxytrichloride, or hexachlorotungsten.

SUB CODE: 11 /

SUBM DATE: 18Apr64

Card 2/2

MARKOVA, V.V.; KORMER, V.A.; PETKOV, A.A.

Addition of organoaluminum compounds by multiple bonds.
Part 2: Addition of diisobutyl aluminum hydride to alkeny-
lacetylenes. Zhur. ob. khim. 35 no.3:447-450 Mr '65.

(MIRA 18:4)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteti-
cheskogo kauchuka imeni S.V. Lebedeva i Leningradskiy
tekhnologicheskoy institut imeni Lenzoveta.

PEREPEL'KIN, O.V.; CHERKASOV, L.N.; KORMER, V.A.; BAL'YAN, Kh.V.

Synthesis and properties of allene hydrocarbon derivatives.

Part 1: Synthesis and properties of alkyl and arylallene
alcohols. Zhur. ob. khim. 35 no.3:574-578 Mr '65.

(MIRA 18:4)

1. Leningradskiy tekhnologicheskii institut imeni Lensoveta.

CHERKASOV, L.N.; KORMER, V.A.; BAL'YAN, Kh.V.

Synthesis and properties of derivatives of allene hydrocarbons.
Part 2: Synthesis and properties of carbocyclic and heterocyclic allene alcohols. Zhur. ob. khim. 35 no.4:616-619 Ap '65.
(MIRA 18:5)

1. Leningradskiy tekhnologicheskii institut imeni Lensoвета.

PEREPELKIN, O.V.; KORMER, V.A.; BAL'YAN, Kh.V.

Synthesis and properties of allene hydrocarbon derivatives.

Part 3: Synthesis and properties of alkyl-, alkenyl-, and
alkynylallene alcohols. Zhur. ob. khim. 35 no.6:957-959

Je '65.

(MIRA 18:6)

1. Leningradskiy tekhnologicheskiy institut imeni Lensoveta.

MARKOVA, V.V.; KORMER, V.A.; PETROV, A.A.

Addition of organoboron compounds to 1,3-enyne hydrocarbons.
Zhur. ob. khim. 35 no.9:1669-1672 S '65. (MIRA 18:10)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo
kauchuka imeni S.V. Lebedeva.

BABITSKIY, B.D.; KORMER, V.A.; LOBACH, M.I.; CHESNOKOVA, N.N.

Role of π -complexes in the coordination-ionic polymerization
of butadiene. Dokl. AN SSSR 160 no.3:591-593 Ja '65. (MIRA 18:3)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo
kauchuka im. S.V. Lebedeva. Submitted July 13, 1964.

L-57011-65 EWT(m)/EPF(c)/EWP(j)/T P-4/Pr-4 RM

ACCESSION NR: AP5010579

VR/0020/65/161/003/0583/0585

AUTHORS: Babitskiy, B. D.; Dolgoplosk, B. A. (Academician); Kormer, V. A.; Lobach, M. I.; Tinyakova, Ye. I.; Yakovlev, V. I.

TITLE: Stereospecific polymerization of butadiene by catalytic systems based on the π -allyl nickel complexes

SOURCE: AN SSSR. Doklady, v. 161, no. 1, 1965, 583-585

TOPIC TAGS: polymerization, butadiene, stereospecificity, nickel organic compound, catalyst

ABSTRACT: The stereospecific catalytic effect of bis-(π -crotyl) complexes of nickel in the polymerization of butadiene was investigated and compared with the effect of π -allyl-Ni complexes. The catalyst was obtained by treating bis-(π -crotyl)-Ni with Ni-halides in a ratio of 1:2. It was found that the catalysts cause the formation of 1-4 polybutadiene, consisting mainly (up to 95%) of cis-1,4-rings, and that the more effective catalysts form in the presence of TiCl_4 . The bis-(π -allyl)-nickel-bromide catalyst caused the formation of polymers in which the number of cis-rings is equal to that of trans-rings, with the formation of 1,2-rings being negligible. Addition of metal halides to bis-(π -allyl)-nickel-bromide and to bis-(π -crotyl)-
Card 1/2

L 52264-65 EPP(c)/EWP(j)/EWT(m)/T—Pc-l/1—1 ESD—RM

ACCESSION NR: AF5010832

UR/0020/65/161/004/0836/0838

AUTHOR: Babitskiy, B. D.; Golenko, T. G.; Kurmer, V. A.; Skoblikova, V. I.;
Tinyakova, Ye. I.; Dolgoplosk, B. A. (Academician)

TITLE: Stereospecific polymerization of butadiene in the presence of catalyst systems based on π -cyclopentadienyl complexes of nickel

SOURCE: AN SSSR. Doklady, v. 161, no. 4, 1965, 836-838

TOPIC TAGS: stereospecific polymerization, polymerization, butadiene polymerization, butadiene, π -complex

ABSTRACT: Polymerization of dienes was studied with catalyst systems composed of π -cyclopentadienyl Ni-complexes and Lewis acids. These systems represent a new group of stereospecific polymerization catalysts as they do not contain compounds with a σ -metal-hydrocarbon bond. Benzene solutions of bis- π -cyclopentadienyl Ni-complex and π -cyclopentadienyl- π -cyclooctadienyl Ni-complexes along with metal halides are effective catalysts for polymerization of butadiene. The solutions of Ni-complexes and of metal halides were prepared separately and were mixed together in an argon atmosphere. Polymerization experiments were carried out at 50°C and

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L 52264-65

ACCESSION NR: AP5010832

the test duration was 17 hours. Butadiene concentration in the total solution was 2.5 mol/l and concentration of metal halides was 5×10^{-3} mol/l. Polymers were precipitated with HCl acidified ethyl alcohol. The yield and molecular weight of the polymers is a function of the type of Lewis acid used and the ratio between individual components of the catalyst system. A $(\pi\text{-C}_2\text{H}_5)_2\text{Ni-TiCl}_4$ catalyst system yielded a polymer containing about 90% cis-1,4 groups, 5 to 10% trans-1,4 groups, and no side vinyl groups. Highest polymer yields were obtained with a Ni:Ti ratio of 1. The polymer molecular weight was not higher than 100,000. The $(\pi\text{-C}_2\text{H}_5)_2\text{Ni-TiCl}_4$ catalyst system yields polybutadiene containing up to 96% cis-1,4 groups. Maximum catalytic activity results from a Ni:V ratio of 1. The molecular weight of polymers is 400,000 to 500,000. The catalyst based on tin-, molybdenum-, and tungsten- yield polymers with 20 to 50% trans-1,4 groups. Depending upon reaction conditions, $(\pi\text{-C}_5\text{H}_5)_2\text{Ni-AlX}_3$ catalysts (where X is Cl or Br) yield polymers with 100 to 50,000 molecular weight. Catalysts based on π -cyclopentadienyl Ni-complexes perform similarly to π -cyclopentadienyl Ni-complexes. The polymers yield polybutadiene containing 10 to 90% cis-1,4 groups. The author is indebted to I. G. Kolokolitseva for synthesis of the bis- π -cyclopentadienyl Ni-complex." Orig. art. has: 2 tables.

Card 2/3

L 52264-65

COLLECTION NR: AP5013832

2
All-Union Scientific Research Institute of Organic Chemistry
N. S. Kurnakov (All-Soviet Institute of Organic Chemistry,
Academy of Sciences USSR)

SUBMITTED 11Dec64

ENCL: 00

SUB CODE: GC, MT

NO REF S: 002

OTHER: 002

BABITSKIY, B.D.; KORMER, V.A.; PODEUBNYI, I.Ya.; SOKOLOV, V.N.; CHESNOKOVA,
N.N.

Tracer method study of the stereospecific polymerization of butadiene
in an aqueous medium in the presence of rhodium chloride. Dokl. AN
SSSR 162 no.5:1060-1062 Je '65. (MIRA 18:7)

1. Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo
kauchuka im. S.V.Lebedeva. Submitted November 30, 1964.

DOLGOPLOSK, B.A., akademik; BABITSKIY, B.D.; KORMER, V.A.; LOBACH, M.I.;
TINYAKOVA, Ye.I.

Link formation mechanism in the stereospecific polymerization
of dienes. Dokl. AN SSSR 164 no.6:1300-1302 O '65.

(MIRA 18:10)

1. Institut neftekhimicheskogo sinteza AN SSSR i Vsesoyuznyy
nauchno-issledovatel'skiy institut sinteticheskogo kauchuka
im. S.V.Lebedeva.

L 13473-66 ENT(m)/ENP(j)/T RM

ACC NR: AP5027842

SOURCE CODE: UR/0020/65/165/001/0095/0098

AUTHORS: Babitskiy, B. D.; Kormer, V. A.; Lapuk, I. M.

ORG: All-Union Scientific Research Institute for Synthetic Rubber im. S. V. Lebedev
(Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka)

TITLE: Polymerization of butadiene by catalysts based on the metal-carbonyls of group VIII metals in periodic table of elements

SOURCE: AN SSSR. Doklady, v. 165, no. 1, 1965, 95-98

TOPIC TAGS: polymer, polymerization, catalytic polymerization, butadiene, nickel compound, cobalt compound

ABSTRACT: The effect of nickel and cobalt carbonyls $Ni(CO)_4$, $Co_2(CO)_8$, $(C_5H_5NiCo)_2$ on the polymerization of butadiene in the presence of different Lewis acids and of AlX_3 , $AlBr_3$, $TiCl_4$, $TiBr_4$, TiI_4 , VCX_4 , $VOCl_3$, $MoCl_5$, and WCl_5 was studied. The polymerization was carried out in benzene or heptane solutions at a temperature of 50°C over a period of 17 hours. The yield of polymer and its microstructure in terms of the fractions of cis- and trans-butadiene monomers in the chain are tabulated. It was found that the catalytic activity of the metal carbonyls and the stoichiometry of the reaction depend on the nature of the Lewis acid. A suggestion is made that the catalytic systems studied here are related to π -allyl and π -cyclopentadienyl nickel.

UDC: 66.095.26+678.762

Card 1/2

L 13473-66

ACC NR: AP5027842

2/

complex systems previously described by B. D. Babitskiy, T. G. Golenko i dr. (DAN, 161, 4, 1965). The authors thank I. A. Zarovaya for participating in this investigation. This paper was presented by academician B. A. Dolgoploskiy on 29 March 1965. Orig. art. has: 1 table and 2 equations.

SUB CODE: 11/

SUBM DATE: 23Mar65/

SOV REF: 003/

OTH REF: 012

Card 2/2

0110-66 EMT(m)/EMP(j)/T INN(c) RM
ACC NR: AP6009488

UR/0020/66/167/001/0099/0101

AUTHOR: Grinberg, A.A. (Academician); Babitskiy, B.D.; Bezhan, I.P.;
Varshavskiy, Yu.S.; Gel'fman, M.I.; Kiseleva, N.V.; Kormer, V.A.; Smolen-
skaya, D.B.; Chesnokova, N.N.

ORG: All-Union Scientific Research Institute for Synthetic Rubber im.
S.V. Lebedev (Vsesoyuzn y nauchno-issledovatel'skiy institut sinteticheskogo
kaukukha); Institute of General and Inorganic Chemistry im. N.S.
Kurnakov of the AN SSSR (Institut obshchey i neorganicheskoy khimii AN
SSSR)

TITLE: The effect of the composition of rhodium(III) complexes on their
catalytic activity in the process of stereospecific polymerization of
butadiene-1,3 in an aqueous medium

SOURCE: AN SSSR. Doklady, v.167; no.1, 1966, 99-101

TOPIC TAGS: rhodium compound, polymerization catalyst, butadiene,
aqueous solution

ABSTRACT: The complexes to be investigated, synthesized by known meth-
ods, were analyzed for their rhodium and halide content. The polymeri-
zation was carried out by methods described in a previous article. A
table shows results of using fifteen different rhodium complexes as
catalysts in the polymerization of butadiene in an aqueous emulsion at
50 and 70°. It follows from these results that the gradual replacement
Curd 1/2

UDC: 66.095.264:678.672:661.897

L 23110-66

ACC NR: AP6009488

of chlorine ions by ammonia molecules leads to a decrease in the polymerization rate. The catalytic activity of bromine derivatives also decreases with an increasing accumulation of ammonia molecules in the inner sphere of the complex. Comparison of the catalytic effect of the halides of rhodium shows that the chlorides and the bromides of rhodium have almost identical catalytic ability and stereospecificity. The iodide is inactive at 50°, while in its presence at 70° there takes place a polymerization process of the free radical type. With the presence of three ammonia molecules in the inner sphere of the iodide the polymerization proceeds by a coordination-ionic mechanism. Results also show that the stereospecific polymerization of butadiene in the presence of the Rh^{3+} complexes studied leads to the formation of trans-1,4-polybutadiene, regardless of the number and nature of the bonds. Orig. art. has: 1 figure and 1 table.

SUB CODE: 07/ SUBM DATE: 12Jul65/ ORIG REF: 003/ OTH REF: 005

Card

2/2